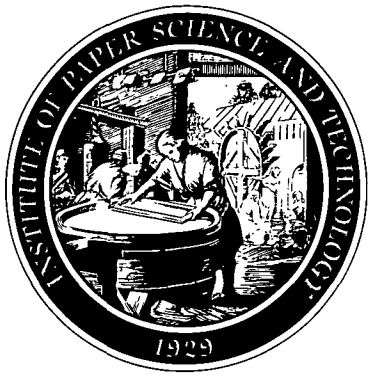

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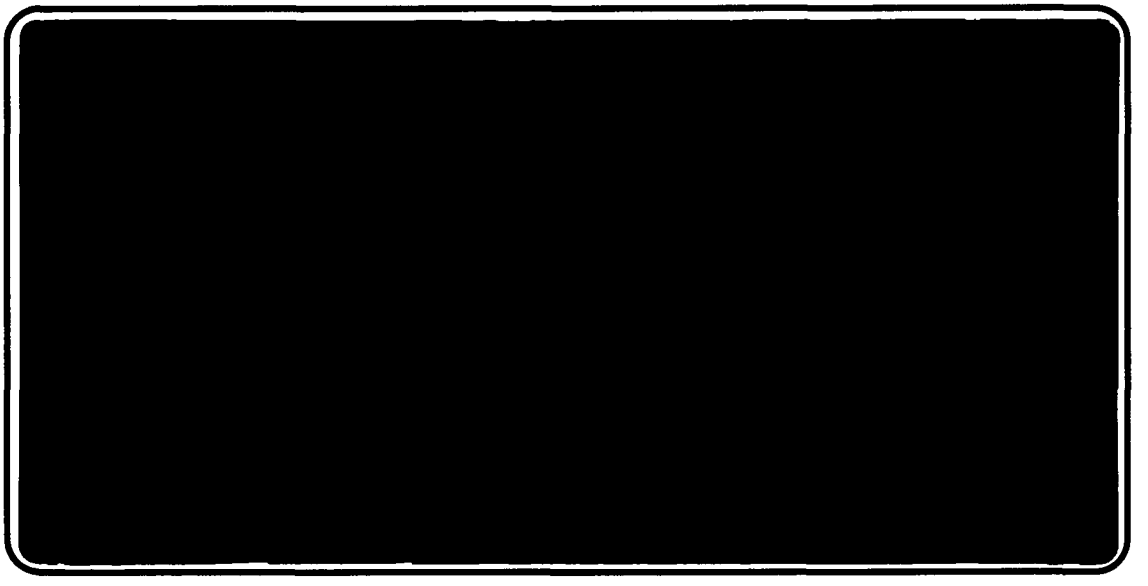

NUMBER 444

THE EFFECTS OF RETENTION AID DISTRIBUTION IN THE FURNISH

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Because the electrostatic charges of the pulp and the filler are usually of the same sign, polyelectrolytes of the opposite charge have been found to be effecive retention aids. For polymers of low charge density the bridging theory developed by LaMer and co-workers (1) provides a reasonable mechanism. The point of addition of the retention aid will determine upon which furnish components the polymer will adsorb. Because polymer adsorption, particularly upon an oppositely-charged surface is virtually irreversible, the distribution between the components is fixed as soon as the adsorption process is completed. Luettgen (2) has recently shown that, for side port injection of polymer into a fiber/filler slurry undergoing turbulent flow, large portions of the stock do not come into contact with the injected polymer solution for several seconds. In another study (3), increasing the amount of agitation at the point of polymer injection improved percent filler retention from 42 to 66. This suggests that the uniformity of distribution of polymer treatment is an important determinant of filler retention.

Other work suggests uneven treatment may be advantageous. Stratton (4) found that adsorption of a polymeric strength aid on only the long fiber fraction resulted in higher strength sheets than when the polymer was distributed across the whole stock or was added to the fines fraction only. Recently, the separate treatment of one or the other of two surfaces on the efficiency of retention (5) and deposition (6) was studied. For a high charge density polymer, Alince (5) found little difference in retention whether the polymer was added to the TiO_2 filler particles or to the fibers. But for a low charge density polyacrylamide, he found percent filler retention in the order: fibers only treated > filler only treated > both treated. He explained his results on the basis of electrostatic interactions between the oppositely charged surfaces of treated and untreated filler or fiber. Varennes and van de Ven (6) studied the deposition and removal of polystyrene latex (PSL) from a flat glass surface. Either or both surfaces were treated with a high charge density, moderate molecular weight cationic polymer. They found greater amounts deposited when the glass surface was treated than when the PSL was treated. During subsequent removal experiments, the strongest particle attachment was shown to occur when both surfaces were treated. The apparently contradictory results of these two studies and the importance of good

retention to papermaking provide the incentive for further examination of the role of polymer distribution among the various surfaces in the furnish.

A model system was designed consisting of fines-free long fiber and monodisperse, spherical filler particles. Experimental conditions for retention evaluation were maintained constant and only the relative proportion of polyelectrolyte supplied to the two surfaces was varied.

Experimental

Materials

A detailed description of the preparation and characterization of the materials has been given elsewhere (7, 8).

Refined cotton linters were classified to remove the fines and then oxidized to increase the carboxyl content to that characteristic of a bleached kraft softwood pulp. The advantage of using cotton is the absence of hemicellulosics in the pulp. The external (hydrodynamic) specific surface area was 1.04 m^2/g determined using the constant flow rate method (9). Total carboxyl content (internal and external) was measured using methylene blue (10) and was 3.1 meq/100 o.d. g (3.0 C/g).

The model filler was a 0.47 μm polystyrene latex whose negative surface charges were a result of sulfate groups. Conductometric titration verified the absence of carboxyl groups and led to a value of the surface charge of 0.058 C/m^2. From the diameter and a density of 1.04 g/cm^3 a specific surface area of 12.3 m^2/g can be calculated.

The retention aid used was a copolymer of acrylamide (95.8 mole %) and methacryloxyethyl trimethyl-ammonium methosulfate (4.2 mole %) with a molecular weight of 2.7×10^6 daltons. The radius of gyration R_g in 0.01 M NaCl was estimated from the work of Mabire et al. (11) to be 100 nm.

All experiments were carried out using distilled water with a background electrolyte concentration of 0.01 M NaCl. This gave a conductivity of 1160 μmho/cm which is in the range of many mill white water systems. The pH was

maintained constant at 6.0 by addition of HCl which allowed most of the carboxyl groups on the fibers to be ionized.

Procedures

A complete description of the procedures has been given elsewhere (7, 8).

Either the fibers or the PSL (or both) could be separately treated with a dilute solution of the retention aid. Addition was made using a special apparatus to maximize so far as possible the uniform treatment of all surfaces. For each experiment 1.2 g fiber and 0.3 g PSL in a total volume of 500 mL were used. Splits of the polymer between the fiber and the PSL were carried out with weight fractions (F) on the fiber of 0, 0.2, 0.33, 0.5, 0.67, 0.8, or 1. In some experiments only a fraction (f) of the PSL was treated with the fraction (1-F) of the polymer. In this case the untreated fraction (1-f) of the PSL was later added to the treated fraction before the total was added to the fibers.

Polymer dosages D of 1, 2, or 3 lb/ton of furnish (i.e., fiber + filler) (0.5, 1.0, or 1.5 kg/tonne) were chosen to give reasonable levels of retention. Because the surface area of the fibers in the furnish is only about 1/3 that of the PSL, we carried out polymer adsorption studies on the fiber at the highest dosage (3 lb/ton) as a function of time. Over 90% of the polymer adsorbed within less than 20 s under our mixing conditions. For the main body of experiments we used adsorption times of two minutes for the fibers and one minute for the PSL; these times were long enough for essentially complete adsorption. An adsorption isotherm of the polymer on the fibers at 120 minutes contact time gave a plateau value (12) equivalent to a dosage of 13.3 lb/ton of furnish. This value might be a little larger at longer contact times (adsorption equilibrium), so the fraction θ of a "monolayer" on the fibers for 3 lb/ton and F = 1 is ≤ 0.23.

After the polymer adsorption step, a sample of the PSL was withdrawn for electrophoretic mobility distribution analysis. The balance was added to the fibers being stirred in a baffled Britt jar. The agitation rate was immediately increased to 750 rpm. After two minutes mixing at this rate, drainage through the screen (76 μm diameter holes) was initiated. Samples of the filtrate were collected for retention analysis and for zeta potential analysis. Retention was calculated from a gravimetric analysis of the oven-dried filtrates with correction

for the NaCl present. When no retention aid was used, PSL retention was less than 1% (or zero within experimental error.) When polymer was present, the confidence interval about the sample mean of replicate experiments was about 8% at a 95% confidence level.

Electrophoretic mobility (EM) distributions were measured using a Malvern Zetasizer 2. Frequency distributions (i.e., fraction of the sample with a given EM) of the white water samples normalized for the amount of PSL retained were subtracted from the corresponding frequency distributions for the PSL before it was added to the fibers. The difference was taken to be the frequency distribution of the PSL retained on the fiber.

Results and Discussion

Electrostatic Effects

Alince (5) explained his retention results on the basis of the interactions of oppositely charged surfaces. We expected similar results with retention being dependent upon the fraction of latex treated and the relative electrostatic charges on the various latex particles and the fibers. We found instead that charge had only a secondary effect.

The average EM of latex (f=1) and of fiber at the different dosages used in this study are shown in Fig. 1. At higher dosages the curve for PSL becomes nonlinear (7) and the isoelectric point (i.e.p.) is reached at 11.2 lb/ton. The results for the fiber were calculated from a study (13) using the same fiber and a polymer with slightly lower charge density (3.0 mole %). For the present system, the assumption was made that the dosage at the i.e.p. was inversely proportional to the polymer's charge density and all dosages were adjusted in the same ratio. Making the crude assumption that the dosage of polymer at the i.e.p. is directly proportional to the surface charge density of the solid, we can calculate the surface charge density of the fiber from that of the PSL to be 0.017 C/m^2 (0.016 C/g). When this value is compared with that of the PSL (0.058 C/m^2), the ratio of the average EM of the two untreated surfaces appears reasonable. This also implies that most of the charge measured by the methylene blue technique resides on interior surfaces of the fiber.

If the retention process is governed by the relative magnitudes and signs of the charges on the fiber and the PSL, we may approximate the interaction by the product of their respective EMs. For the different splits of polymer dosage, the EM of the treated PSL was measured directly before adding it to the fiber, and that of the fiber was estimated from the curve in Fig. 1. The correlation is shown in Fig. 2 where a negative or positive value on the abscissa indicates interactions between oppositely- or like-charged surfaces, respectively. We find relatively good retention under conditions where both surfaces are negatively charged, as well as when the fiber is positively charged and the PSL is negatively charged. Separate curves are found for each dosage, which appears to be a more important determinant of the retention. This result is in agreement with the short Debye screening length (κ^{-1} = 3.0 nm in 0.01 M KCl) which governs the range of electrostatic interactions and with the use of a low charge density, bridging-type polymer. The "tails" of the latter could extend beyond the Debye length and promote retention. Further analysis below lends support to this picture.

Even though the PSL is monodisperse in diameter, EM measurements indicate an apparent distribution of number of charges on a population of particles. When the particles are treated with the retention aid, the distribution broadens suggesting an uneven distribution of the polymer among the particles. Analysis of the EM distributions shows that a certain fraction of the population is preferentially retained. The mean EM of this fraction is dependent on the corresponding mean value of the fibers. The results for two experiments that illustrate this behavior are given in Table 1. At this level of polymer dosage (1 lb/ton) all surfaces remain negatively charged. However, as the fibers become less negative (greater proportion of polymer on the fibers), the species of PSL retained shifts to more negative values. This is shown visually in Figs. 3 and 4 where the darker bars represent the EM values for the retained PSL, the lighter bars the white water values, and the sum of the two the headbox values. (The "headbox" sample is measured before the PSL is added to the fibers.) Note that the mean values for the EM of the headbox and white water samples in Table 1 are not equal. The headbox sample is less negative than the white water sample for the first experiment, while the reverse is true for the second. The difference between the mean EM values for the retained PSL particles for the two experiments is large. Contrary to popular belief, the sample with the more

negative headbox (or white water) EM produces the higher retention. These results suggest that, while electrostatic interactions influence retention, other factors may be more important for bridging-type polymers.

Table 1. Electrokinetic results at various locations.
(Overall polymer dosage is 1 lb/ton)

		Electrophoretic Mobility, (μm/sec)/(volt/cm)					
		Fiber	PSL				
F	f	Fiber	Treated fraction	Headbox*	White water	Retained	Retention, %
0.20	0.75	-0.8	-4.9	-5.2	-5.4	-4.8	30
0.67	1.00	-0.4	-6.0	-6.1	-5.8	-6.4	47

*before addition to fibers.

Retention Aid "Tail" Effects

"Bridging" depends upon the ability of an adsorbed macromolecule to span the electrical double layers of its adsorbent and that of the particle to which it will bridge, or approximately twice the Debye screening length. For high molecular weight polymers, Scheutjens et al. (14) have shown that the tails of the chains are the major contributor to the hydrodynamic layer thickness when crowding effects between adsorbed molecules become important. The retention results offer further evidence for this.

In the discussion that follows, at a constant value of fiber dosage FD, we have averaged the results for variable fraction of the PSL treated (i.e., f = 0.2, 0.5, 0.75, or 1.0). The standard deviation for the retention at the four values of f varied from 2 to 15 for 15 different values of FD. The average value of these standard deviations was 7 with a standard deviation of the standard deviations of 4. This means that, within the experimental error of the retention determination, differentiation could not be made between the case where all PSL particles received equal access (i.e., f = 1) to the polymer dose (1-F)D and the case where only a fraction (f < 1) of the particles received that dose. There was no observable trend of dependence of retention on fraction f of PSL treated at

constant dosage (1-F)D. Perhaps with greater experimental precision in the retention measurement such a trend could be discerned. However, to a first approximation we may say that the distribution of the retention aid among the filler particles is of minor importance.

Retention of the PSL is plotted in Fig. 5 against the dosage of the polymer on the fibers FD as a function of the overall dosage to the furnish D. Even though the PSL is negatively charged in each case and the charge on the fiber goes from negative to positive with increasing dosage (Fig. 1), the curves at constant dosage exhibit maxima. The solid lines are smooth curves whose purpose is merely to guide the eye.

Consider first the cases where the retention aid is either all on the PSL or all on the fibers. The point at zero dosage on the fibers represents the average of 12 experiments (3 levels of retention aid dosage x 4 values of f). The mean of these 12 values was 9% with a standard deviation of 6. Again, no trend with fraction treated f was discernible. Also, no effect of the level of polymer treatment (1, 2, or 3 lb/ton) was found within experimental error, even though there is a strong effect of polymer dosage on the EM of the PSL (Fig. 1). On the other hand, the effect of increasing polymer dosage when only fibers are treated (F=1) is large. The dashed line in Fig. 5 is a least squares fit of the hyperbolic tangent function to these values including the point at zero dosage which showed zero retention. It might be argued that the large increase in retention when the dose on the fibers is increased from 1 to 2 lb/ton is a result of the change from negative to positive charge on the fibers (Fig. 1), but this does not explain the maxima in the curves nor the insensitivity of filler retention to dosage when only the PSL is treated.

A more plausible explanation concerns the effect of polymer dosage on the extension of adsorbed polymer tails from the fiber surface. For interactions between spheres and cylinders, van de Ven (15, 16) has shown that in the absence of colloidal forces the spheres (filler) would follow a closed trajectory around the (circular) periphery of the cylinder (fiber) without becoming attached. For this trajectory there is a distance of minimum approach; the bridging polymer must be able to span this distance for retention to occur. Obviously, greater tail extension will promote attachment. In the following discussion, we make the

This equation describes the filler retention attributable to the tail extension and includes the possibility of only a portion f of the filler being treated with polymer. The "tail function" T_{filler} describes the tail extension, S is the specific surface area of the filler, and the other symbols have their previous meaning.

Equations 1-4 can be used to predict the contributions to retention of the tail extension as a function of surface concentration of polymer. They do not predict the maxima found in Fig. 5 and, in fact, for a dosage of 1 lb/ton predict less than 1% retention at FD = 0.5. (It is of interest that the maximum retention found at this dosage is 41 %, equal to R_m.) Clearly, when both surfaces are treated, retention is greatly enhanced as shown previously by Varennes and van de Ven (6). We may make the simple assumption (following the concepts of LaMer and co-workers (1) concerning flocculation) that the amount of retention will be proportional to the product of the fraction of the polymer applied to the fiber F and the fraction applied to the PSL (1 - F). We further note that Hogg (18) has suggested that the collision efficiency is equal to twice this product to account for all possibilities of interaction between the two surfaces. Thus, the retention due to interaction between fiber and filler when both are treated with polymer is given by

$$R = 2\,C\,F\,(1\text{-}F)\,R_m \qquad (5)$$

R_m has its previous value and C is a constant to provide equality between R and R_m at F = 0.5 with the value 2.0 here. Although this equation predicts a maximum for retention as a function of F, it predicts zero retention for F = 1 and 0. As already noted, we find significant retention at F = 1 and finite values at F = 0.

These results suggest that a linear combination of eqs. 2, 4, and 5 would enable us to describe retention over a wide range of conditions.

$$R = R_m\,[2\,C\,F\,(1 - F) + F\,T_{fiber} + f\,(1 - F)\,T_{filler}\,] \qquad (6)$$

Here, the first term describes interactions between fiber and filler when both are treated with polymer. The second and third terms describe the increase in tail extension due to increasing surface concentration of the polymer. All three terms

assumption that filler retention is directly proportional to the extension of the polymer tails from the surface. The data from Fig. 5 for F = 1 are replotted in Fig. 6 (as closed circles) in units of surface concentration using the hydrodynamic specific surface area of the fibers and assuming 100% of the polymer has adsorbed. For comparison the circular area projected on the surface of a molecule having a diameter of 2 R_g (= 200 nm) is shown by the arrow. Already at a dosage of 1 lb/ton, an adsorbed molecule is compressed to an area about 1/4 that corresponding to its size in solution before adsorption. Fleer et al. (17) predict that the hydrodynamic thickness δ_H, which is largely controlled by the tails, depends on surface concentration in a similar manner to the curve in Fig. 6. Also shown in Fig. 6 are the data (open circles) for the experiments where F = 0 (only PSL is treated). Again, the surface concentration is calculated assuming 100% adsorption of the polymer on the fraction f of the PSL surface corresponding to the particular experiment. Also, the experimental retention value is divided by the fraction f because of the reasonable assumption that only those particles which have been treated can become attached to the (untreated) fiber surface. The data for the most part appear to follow the same relationship as do those when polymer is adsorbed to fiber only. The points falling far from the curve may be attributed to experimental error and the fact that the experimental retention is on the order of 10% or less for these samples. The fact that the results for PSL, having a surface charge density about 3.4 times that of the fibers, fall on the same curve as those for the fibers is not surprising. Theory (17) predicts that beyond about 1.5 χ_{sc}, where χ_{sc} is a critical adsorption energy, further increases in the adsorption energy have little effect on the hydrodynamic thickness or the tail length. Since the interactions between the cationic polymer and the anionic surfaces are ionic, the adsorption energies would be expected to be much larger than the critical adsorption energy.

The value of the maximum retention found when only one surface is treated (41%) may be a result of reaching the maximum tail extension for the given molecular weight as predicted by theory (17) for increasing surface coverage. Alternatively, it may be an indication of "blocking." If circles are placed on a surface with uniform triangular spacing, the maximum area covered with increasing number of circles before overlap occurs (Fig. 7) is $(\pi/18)\sqrt{3}$. For our furnish with 20 weight % of PSL and accounting for the specific surface areas of the fiber and filler, the critical retention when overlap occurs is 41%. This may be

merely coincidental. Such regular packing would not be expected here because the lateral repulsion between adsorbed PSL particles due to electrostatic forces would be effectively screened by the background electrolyte (Debye length of only 3 nm). At 100% retention in our furnish 81.5% of a hexagonally close-packed monolayer would be achieved, so there would be room for all the particles to fit on the fibers in a monolayer if the particles could move laterally to accommodate each other. Yet another explanation for the "leveling off" of retention may involve desorption of PSL due to the hydrodynamic flows (6) in the Britt jar. Further investigations to resolve this question might include increasing the polymer's molecular weight to increase the tail length (14), varying the PSL size to change the projected area per unit mass of filler, and varying the hydrodynamic conditions in the Britt jar.

The curve for the data in Fig. 5 (only fibers treated) can be generalized as

$$\% R = F R_m \ (1/2)\{1 + \tanh[a(DF/pS_W - b)]\} \quad (1)$$

$$= F R_m T_{fiber} \quad (2)$$

where R_m is the maximum value of retention found when only treating one surface, p is the weight fraction of the fiber in the furnish (here, 0.8), and S_W is the hydrodynamic specific surface area. The constants R_m, a, and b are obtained by fitting the data to the hyperbolic tangent function. The constant a is related to the rate of change in tail length with surface coverage which depends on molecular weight (17), while b defines the surface concentration where the extension of the tails is occurring most rapidly and depends on the polymer-solvent interaction parameter χ (17). The "tail function" T_{fiber} which has a range from 0 to 1 denotes the fraction of the maximum extension of the tails at a particular dosage condition. (The hyperbolic tangent function is used here for convenience only and has no theoretical basis.) For the filler a similar equation holds.

$$\% R = (1-F) R_m f (1/2)\{1 + \tanh[a(D(1-F)/f(1-p)S - b)]\} \quad (3)$$

$$= (1-F) R_m f T_{filler} \quad (4)$$

contribute when both surfaces are treated. When only fiber or filler are treated, the second or third term, respectively, contributes.

The physical picture is that, when only one or the other of the surfaces is treated, the retention is governed by the extension of the tails. When both surfaces are treated, the extension of the tails contributes, but there is also a synergistic interaction between fiber and filler which leads to enhanced retention. Thus even when the extension is minimal (e.g., for D = 1 lb/ton), collisions between fiber and filler lead to significant retention.

This equation was tested using the data in Fig. 5. Since our retention data could not differentiate between different fractions f of PSL treated and are average values, we set f = 1 in eqs. 3 and 6. Recall that there is only one adjustable parameter C obtained from the fit to eq. 5 at F = 0.5 and a dosage of 1 lb/ton (where the contributions from tail extension are negligible.) The other constants a, b, and R_m are obtained from the fit of the hyperbolic tangent function to the data for F = 1 in Fig. 5. The results are shown in Fig. 8 where reasonable agreement is found between the experimental values and the theoretical predictions. The contributions of the different terms in eq. 6 are shown in Fig. 9 for the case where the dosage is 2 lb/ton. The first term contributes the most except at high fractions F where the effect of the tail extension becomes important. Further work is needed over a broad range of variables to ascertain the general applicability of eqs. 1 - 6 and to provide the basis for a better physical picture of the interactions leading to eq. 5.

Conclusions

Electrostatic charge effects influence which filler particles are retained, but cannot by themselves be used to predict retention. The concept of adsorbed polymer tail extension can be used to interpret the retention results. A simple theory including the effects of tail extension and of the interaction between fiber and filler when both possess adsorbed polymer is successful in predicting retention.

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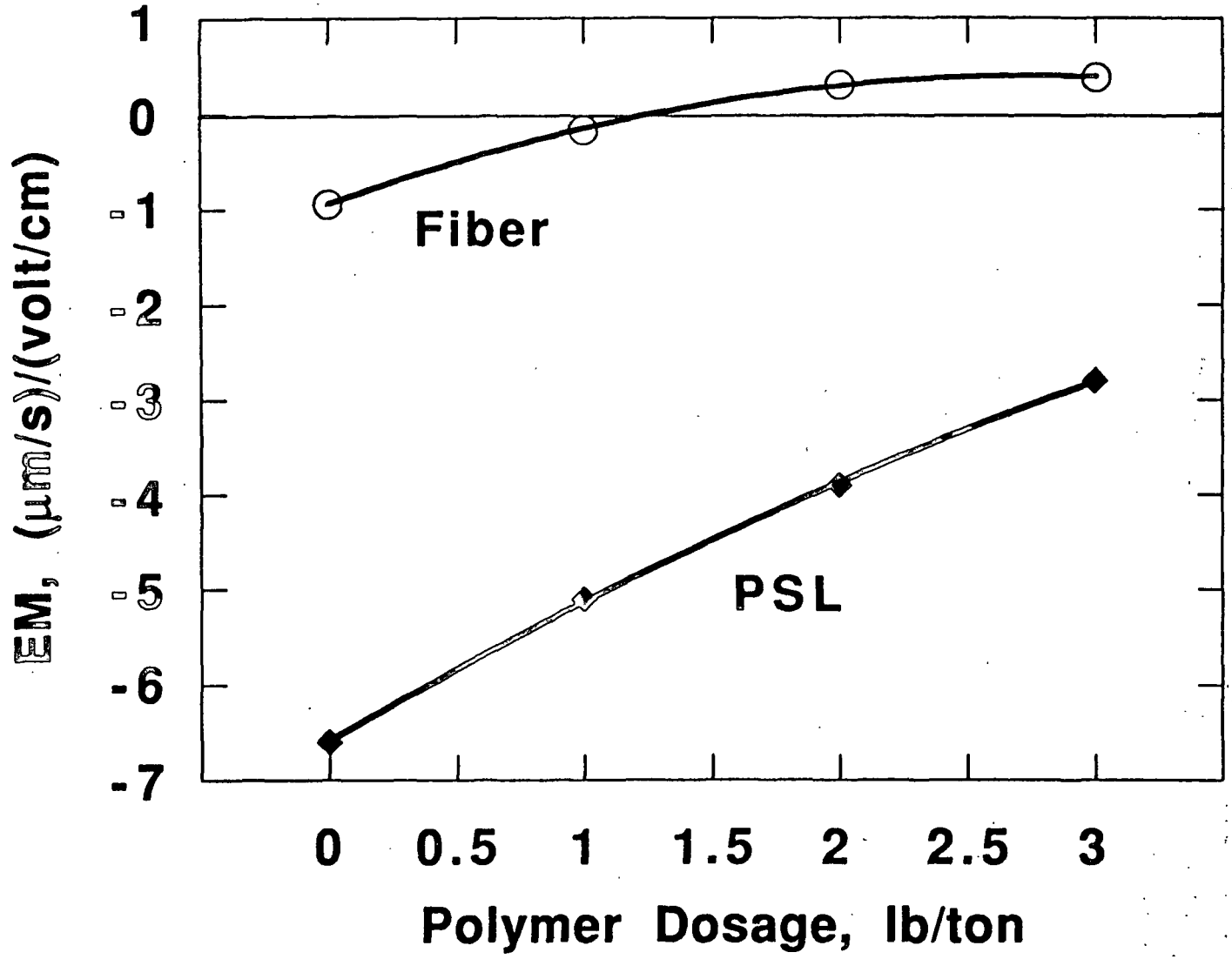

Fig. 1. Dependence of the individual EM of the fiber and filler as a function of polymer dosage calculated on the basis of the total amount of furnish.

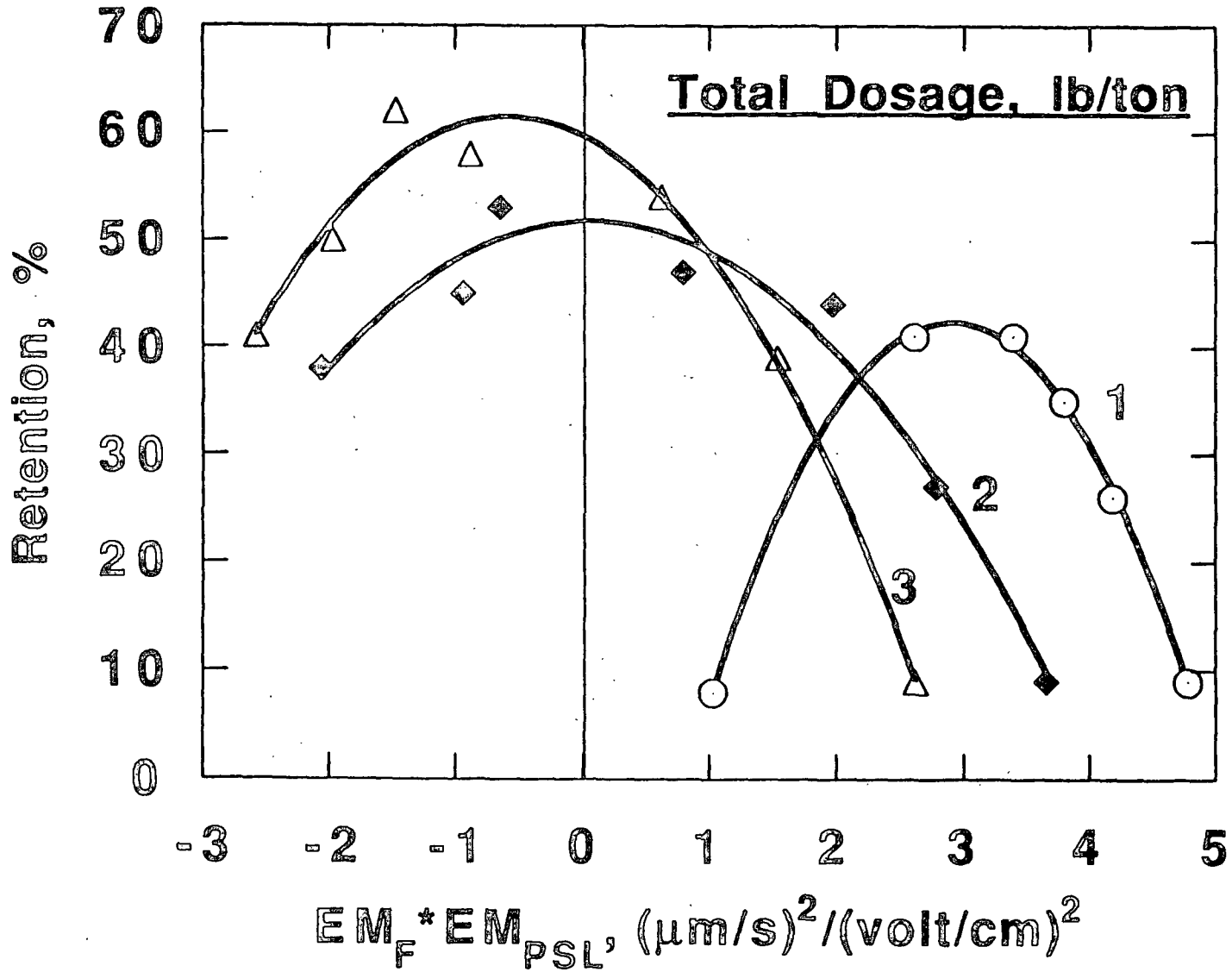

Fig. 2. Dependence of retention on electrostatic interactions as a function of overall polymer dosage.

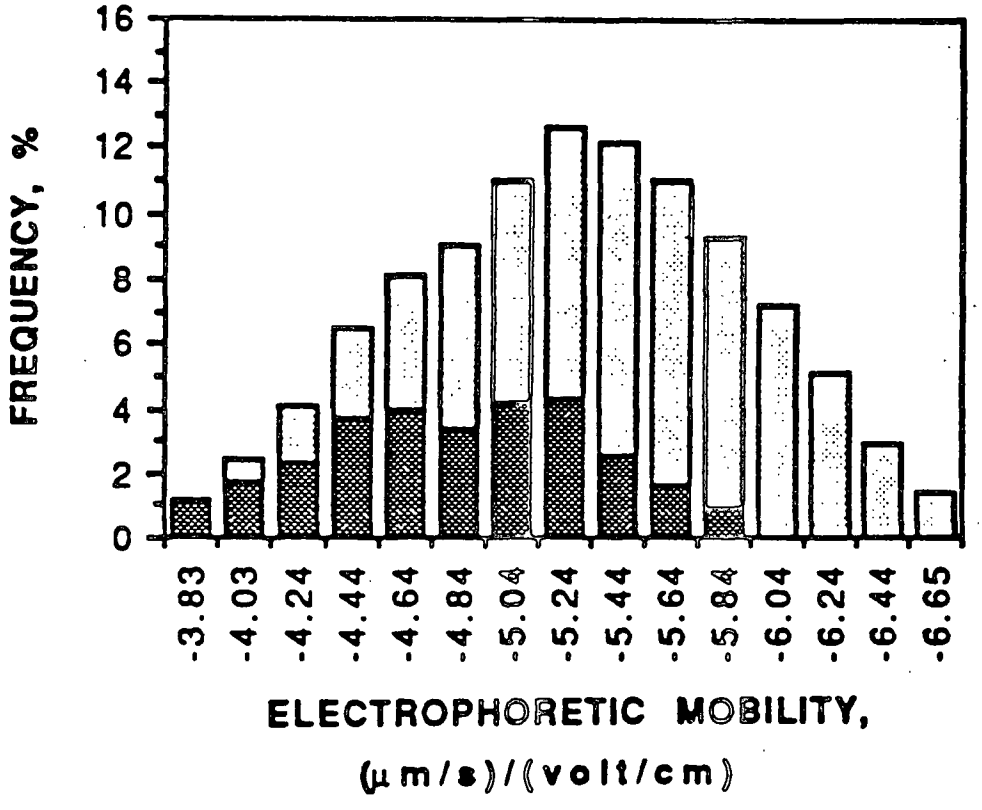

Fig. 3. Distribution of EM for an experiment with D = 1 lb/ton, F = 0.2, and f = 0.75 showing the preferential retention of the least negative PSL particles.

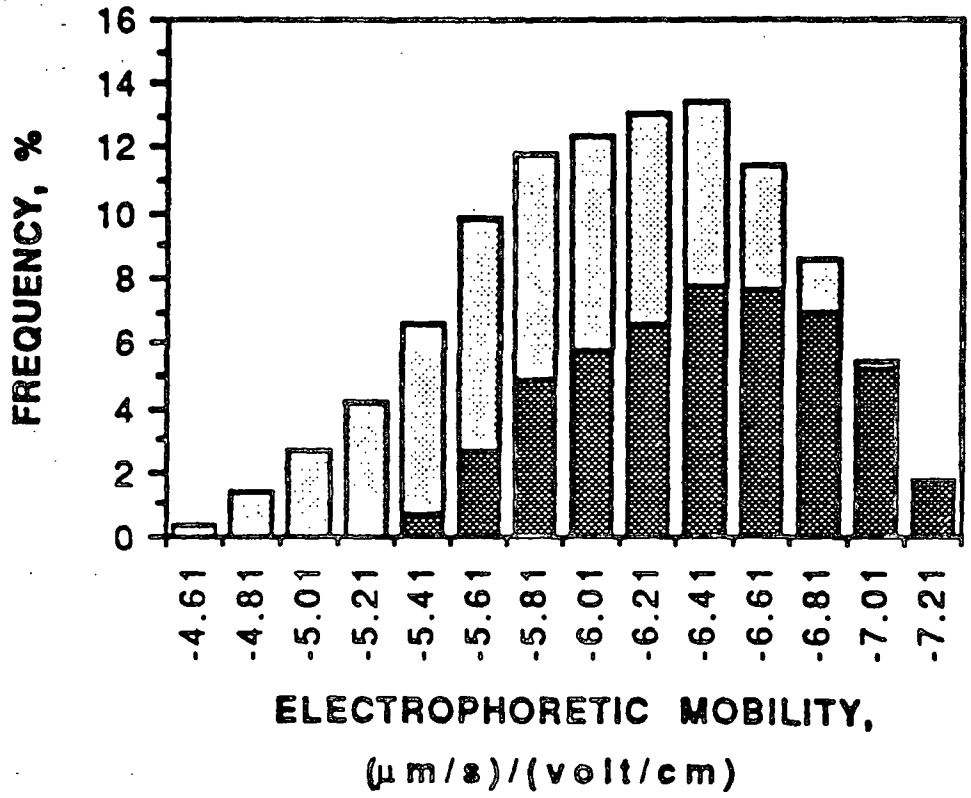

Fig. 4. Distribution of EM for an experiment with D = 1 lb/ton, F = 0.67, and f = 1.0 showing the preferential retention of the most negative PSL particles.

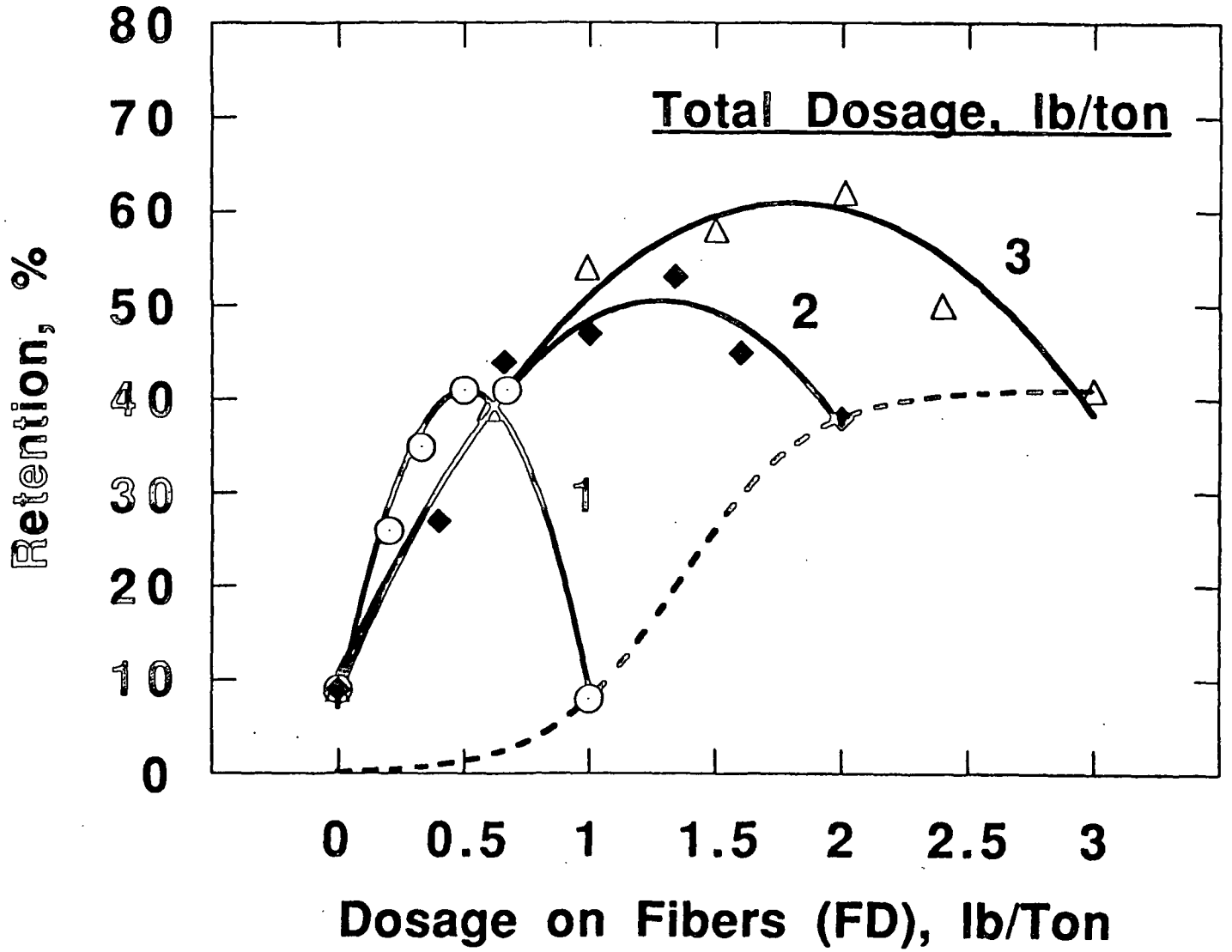

Fig. 5. Retention as a function of the dosage on the fibers at various levels of overall polymer dosage. The dotted curve is a least squares fit of the hyperbolic tangent function to the data with F =1.

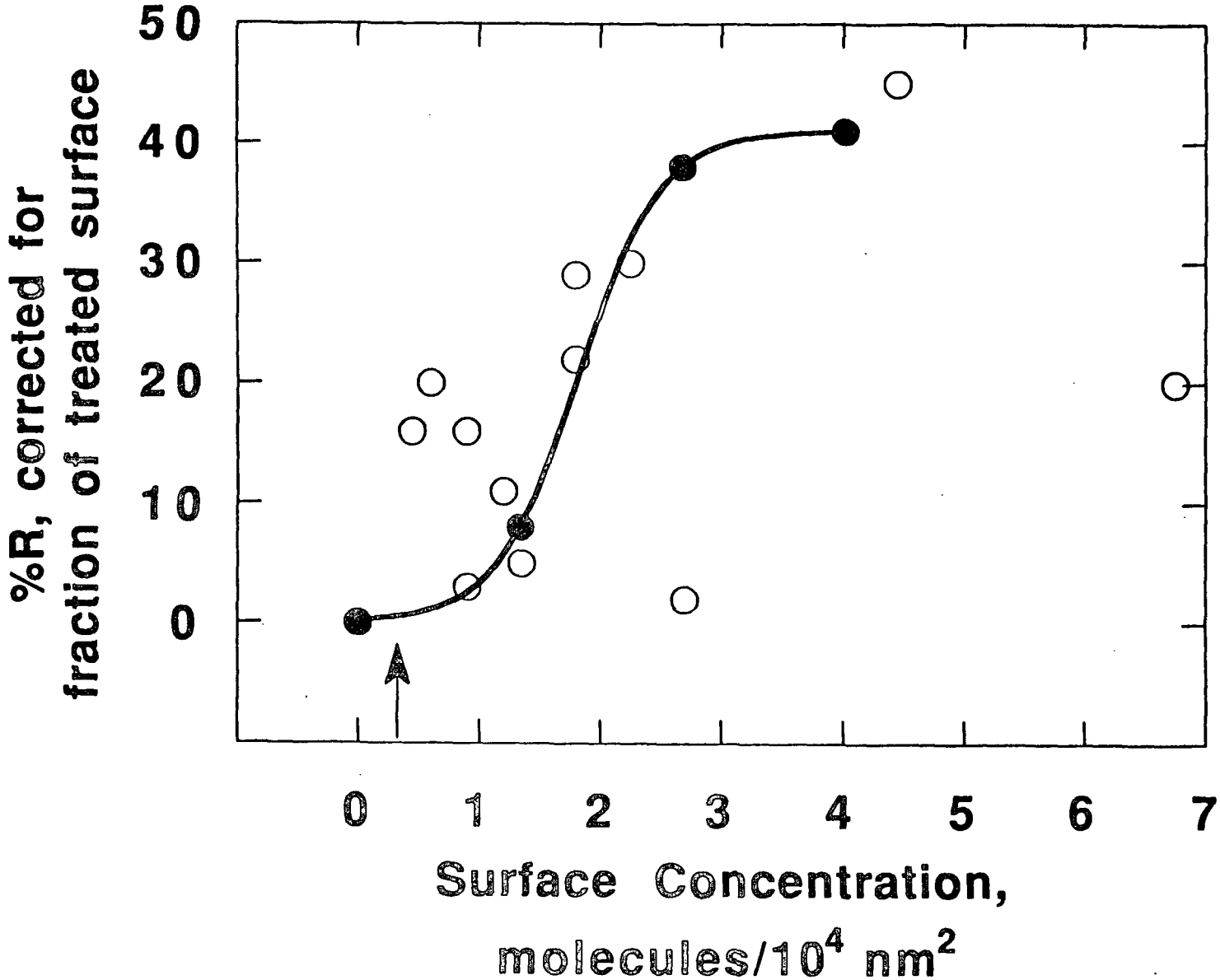

Fig. 6. Effect on retention of the surface concentration of polymer. Closed circles, polymer on fibers only; open circles, polymer on PSL only. Arrow indicates the concentration corresponding to the projected area of a molecule in solution (diameter = 2 R_g).

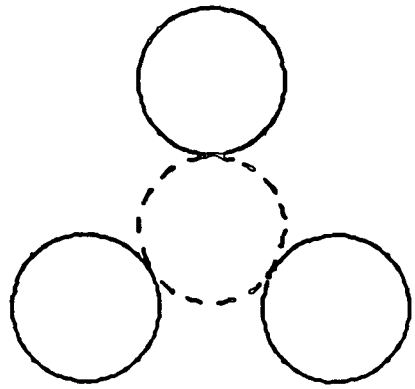

Fig. 7. Diagram showing the maximum packing on a hexagonal lattice before overlap occurs.

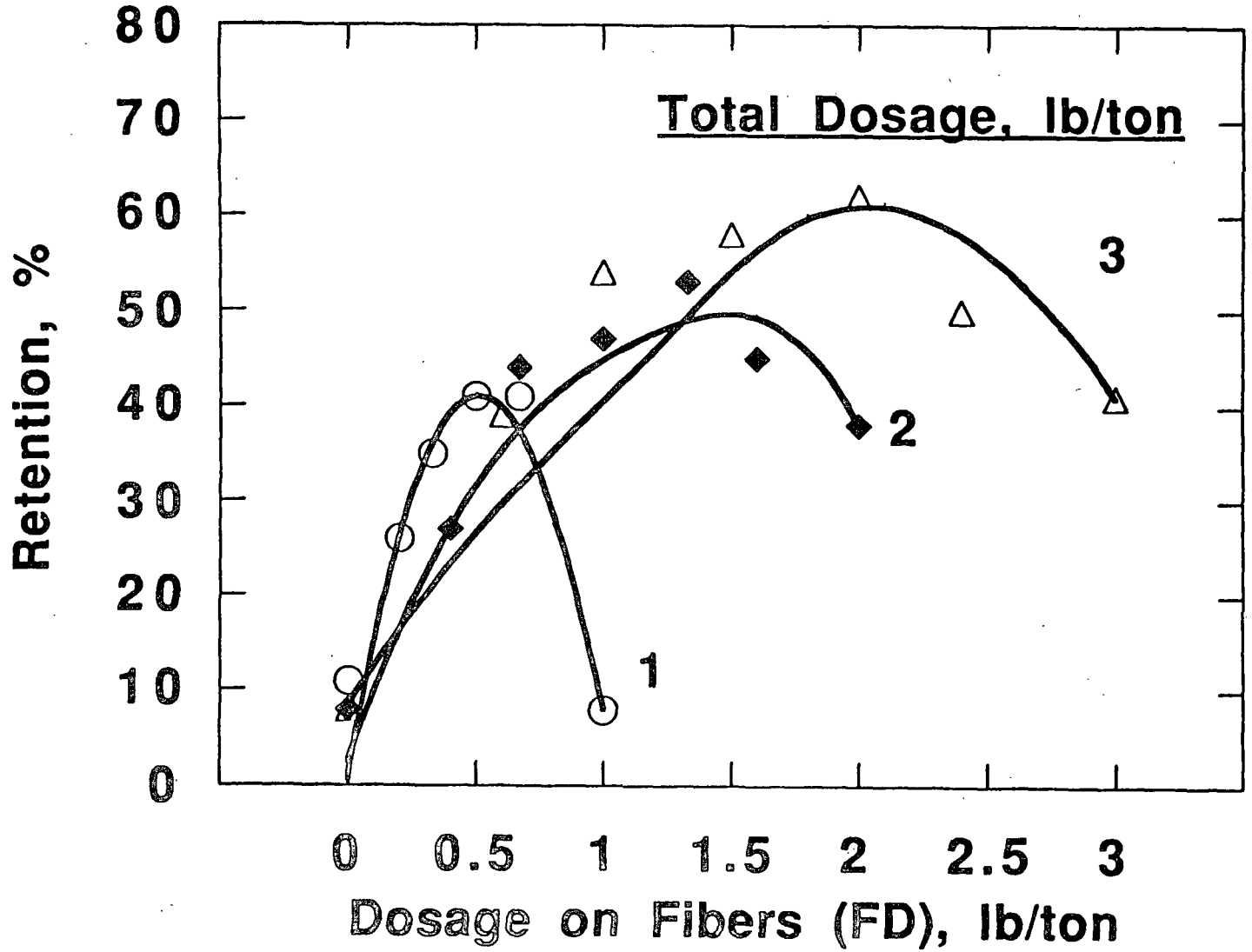

Fig. 8. Retention as a function of the dosage on the fibers at various levels of overall polymer dosage. The curves are calculated from eq. 6.

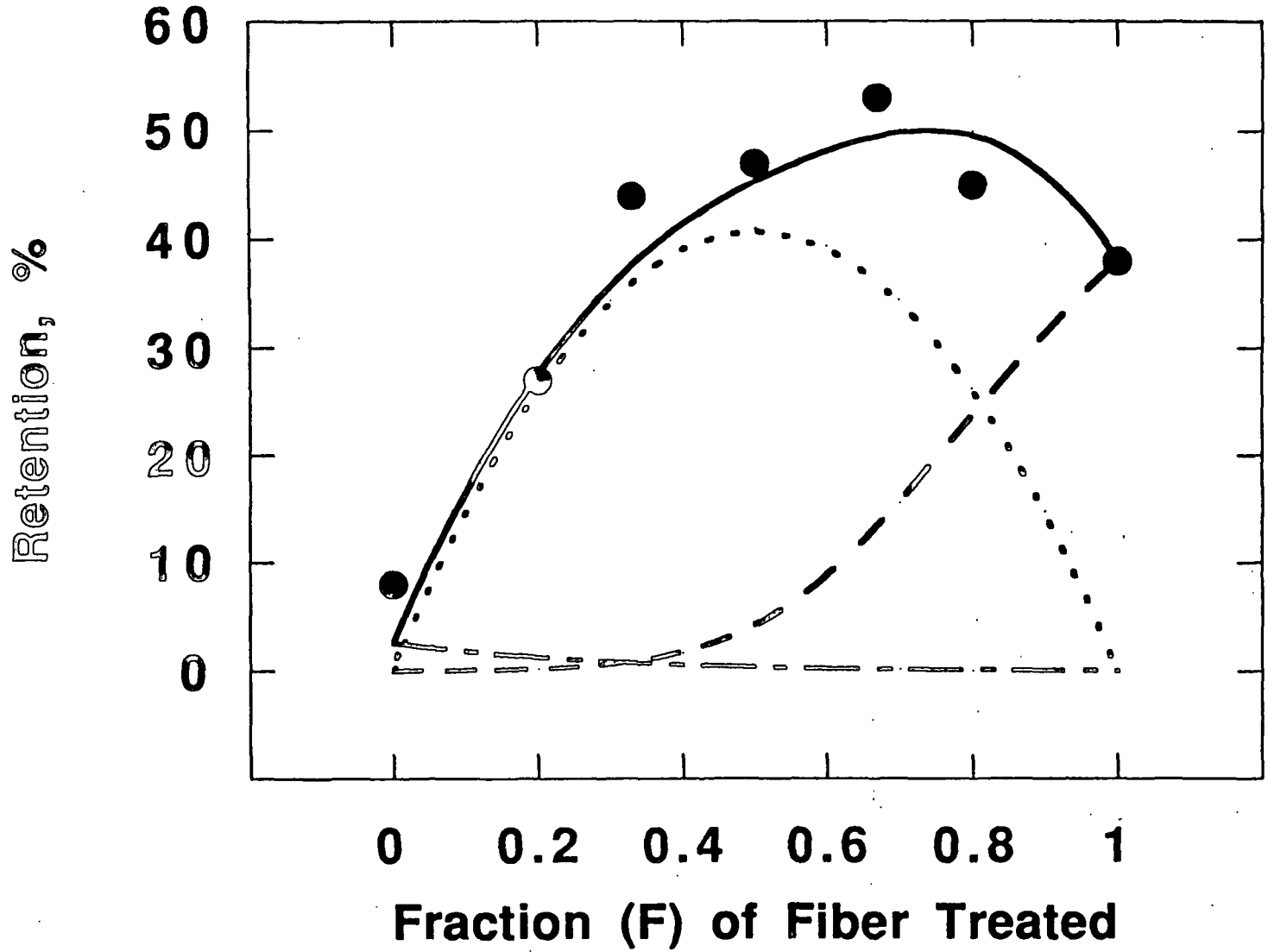

Fig. 9. Illustration of the contribution of the various terms in eq. 6 to retention for a dosage of 2 lb/ton. Dotted curve, first term; dashed curve, second term; dot-dashed curve, third term; solid line, sum of the 3 terms; closed circles, experimental data.